

DEVELOPMENT OF NEW SEALED BIPOLAR LEAD-ACID BATTERY

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New light weight composite bipolar plates which can withstand the corrosive environment of the lead-acid battery have made possible the construction of a sealed bipolar lead-acid battery that promises to achieve very high specific power levels and substantially higher energy densities than conventional lead-acid batteries. Performance projections based on preliminary experimental results show that the peak specific power of the battery can be as high as 90 kW/kg, and that a specific power of 5 kW/kg can be sustained over several thousand pulses.

I. INTRODUCTION

A program for the development of a 50-kW sealed bipolar lead-acid battery is currently underway at JPL, under the sponsorship of the Air Force Wright Aeronautical Laboratories. This three year program which started in July 1987 is in competition with three other programs using other electrochemical couples, all aiming at the development of 50-kW batteries by the end of 1989. At that time a single system will be selected for the construction of a 100 Megawatt battery.

II. BACKGROUND

Two distinct designs of the sealed bipolar lead-acid battery are under development. One of the designs is based on a bipolar battery developed by TRW for the Environmental Protection Agency (EPA) in 1972 [Ref. 1]. That battery utilizes bipolar plates made of a polymeric matrix filled with vitreous carbon and bonded to a thin lead sheet; our contractor for that system is Gates Corp. The other design which is the subject of this paper grew out of several years of JPL's involvement in the Electric & Hybrid Vehicle Project of the Department of Energy; the key elements of this new bipolar design are sealed construction, a light-weight composite bipolar plate made of conductive glass and carbon fibers embedded in a polymeric matrix, and the addition of tin dioxide coated glass fibers to the positive active material. A contract for the development of this new battery has been awarded to ENSCI, Inc. in Chatsworth, California.

III. DESCRIPTION OF SYSTEM

a. System Design

This new lead-acid battery designed for high power applications is unusual in that it is a bipolar battery with sealed design. Figures 1 and 2 show diagrams of the bipolar stack and the sealed battery respectively. The requirement of maximum specific power dictates a bipolar construction in order to eliminate resistance through the grid and the active mass. For any application either terrestrial or space, such a battery needs to be sealed, as watering would be impractical because of the large number of very thin cells required.

b. New 2-Layer Light-Weight Plastic Composite Bipolar Plate

Lead has been the commonly used material for the bipolar plate in previous lead-acid batteries [Ref. 2], but the weight of lead is unacceptable in minimum practical thicknesses. The battery described here uses a plastic composite for the bipolar plate, in which the conductors embedded in the plastic matrix are tin dioxide coated glass fibers on the positive side of the biplate and carbon fibers on the negative side. This light weight composite biplate is currently being manufactured by ENSCI, under a contract with JPL. Table 1 shows recent results obtained by ENSCI for several biplates; the most recent versions of the bipolar plate have a thickness of 20 mils, a volume resistivity of 2 ohm-cm and an area density less than 0.1 g/cm². With the use of thermoset resins for the polymeric matrix the open porosity of the bipolar plate is essentially eliminated.

The bipolar plate is manufactured using conventional polymeric composite technology. Both thermoset and thermoplastic resins have been used with equal success, but better results are obtained for very thin bipolar plates with the thermoset resins. The carbon fibers are commercially available, whereas no commercial source of tin dioxide coated glass fibers is available at the present time. Currently, the thin conductive stannic oxide films on the glass fibers are produced by spraying a solution of tin tetrachloride in the presence of air on a heated glass fiber mat. This process, known as spray pyrolysis [Ref. 3], has long been a production method for applying transparent SnO_x conductive thin films to glass. Figures 3 and 4 show photomicrographs of glass fibers of 10 micron diameter, coated with 1 micron of conductive tin dioxide. At the present time, the process variables are well under control, but the production rate is low.

Corrosion tests indicate that while SnO₂ is thermodynamically stable with respect to oxidation and thermodynamically stable with respect to reduction at the positive electrode in normal operation, it is subject to reduction during reversal of that electrode [Ref. 4]. The material will never be life-limiting when used in the positive plate environment, providing only that care

be taken to prevent reversal of the positive plates.

c. Conductive Glass Fibers in Positive Active Material.

In this new battery design, the conductivity of the positive active material (PAM) is enhanced by the addition of the stannic-oxide coated glass fibers. The use of these conductive fibers in the PAM is especially important as the state of charge of the battery declines. Figure 5 shows the per cent positive active material utilization as a function of discharge rate with and without the addition of the fibers. A 75 % increase in utilization at the 1-hour rate of discharge is observed in cells with the fibers.

IV. ADVANTAGES

a. High Specific Power

The fundamental advantage of the lead-acid couple for high power applications is due to three characteristics: high open circuit voltage, low electrolyte resistivity, and discharge with an increase in entropy. Very few couples can match the ratio of the square of the open circuit voltage to electrolyte resistivity of the lead-acid couple and most couples discharge exothermically (see Table 2). For the lead-acid battery, the change in entropy makes the reversible component of heating negative on discharge. This heating must therefore be positive on charge but charge rates are very low compared to discharge rates. Furthermore, the sealed bipolar lead acid battery described above has the advantages of very light weight construction and a thermodynamically stable conductor in the bipolar plate.

The specific power, in kW/Kg, can be factored into two parts: the surface power density, in W/cm², and the specific area, in cm²/Kg. Batteries very often do well on one of these factors but fail to show a high specific power because of doing poorly on the other.

The maximum surface power density, P_{smax} , of an electrochemical cell is given by

$$P_{smax} = \frac{P_{max}}{A} = \frac{(E'_{oc})^2}{4RA} \quad (1)$$

where P_{max} is the maximum total power, A is the plate area, E'_{oc} is the battery open circuit potential extrapolated to zero current from the polarization curve, and R is the total internal resistance. If the electrolyte resistance dominates the battery resistance, and l is the thickness of the electrolyte between the plates (separator thickness) then

$$P_{smax} = \frac{(E'_{oc})^2}{4rl} \quad (2)$$

where r is the electrolyte resistivity. For comparison purposes P_{max} for an electrochemical cell can be expressed as a figure of merit (M) as given by

$$M = \frac{(E'_{\text{oc}})^2}{r} \quad (3)$$

which allows a comparison to be made among various battery couples to predict the ones most capable of having the highest surface power densities. The figure of merit, M , is calculated for nine different couples in Table 2. The values of E'_{oc} (except for Na-S and Li-FeS) were extrapolated from E - I curves in the literature and those for r were from the battery literature. The lead-acid system based on the intrinsic properties of the couple alone has 3 times the Ag-Zn and more than 4 times the Ni-H₂ and Ni-Cd surface power density.

Table 2 also shows the calculated quantity Q/E which is the ratio of thermal to electrical energy when discharging at $2/3 E'_{\text{oc}}$. The values for the Q/E ratio are consistent with those projected from thermodynamic considerations. The lead-acid system appears to be optimum.

The specific area of this new battery is also high due to the multistack bipolar construction, the lightweight composite plastic bipolar plate (0.1 g/cm^2), and the lack of need for auxiliary equipment such as pumps, cooling loops, and heavy storage containers required by the other systems.

b. The use of conducting tin oxide coated glass fibers in the positive active material (PAM) is another distinguishing feature of this battery. Lead dioxide makes an unusually low resistance contact with the stannic oxide and the contact resistance appears to be unchanging with time or state of charge. The benefit for a very high pulse power requirement is that these conductive fibers will enhance conduction in the positive plate and that this conduction will reduce the usual power decline with decreasing state of charge. Additional benefits expected from the presence of a stable conductor within a few microns of all parts of the PAM are: longer cycle life because of reduced morphological degradation, rapid and total formation in all cases, and very high utilization of the positive electrode. This last effect was repeatedly demonstrated by scientists at ENSCI who consistently measured utilization efficiencies in excess of 40% at the 1 hour discharge rate (see Figure 5).

V. PERFORMANCE PROJECTIONS

Performance estimates for the sealed bipolar lead-acid battery have been made for a number of different discharge modes. These include constant current discharges to depletion of capacity of 1, 5, 10, and 100 seconds and pulse discharges of 5 msec per pulse at 5 Hz for 1000 seconds. The estimates based on

preliminary information on the physical characteristics of the bipolar plate are shown in Figure 6. A full description of the design and operational variables for the battery will be the subject of a paper currently in preparation, to be presented at the 22nd IECEC meeting in Philadelphia, August, 1987.

A battery of specified power output would have a size dependent upon the time allotted for its complete discharge. The size and shape of the battery would also be determined in part by its voltage. Based upon the characteristics known about the battery at this time it is calculated that a 50 KW battery of a nominal 100 Volts would have approximately the characteristics shown in Table 3.

VI. PERFORMANCE CHARACTERISTICS OF TEST CELL

A test cell consisting of the two end electrodes of a bipolar battery was recently assembled and tested at JPL. In this cell, the end electrodes, approximately 15 mils thick, are pasted onto a 1/4 inch thick pure lead disk, 2 inches in diameter, which acts as a current collector. The cell has an active electrode area of 5 cm^2 and a theoretical capacity of 200 mAh assuming 100% utilization.

The cell was tested at various rates of discharge ranging from 1 second to 15 minutes. Figure 7 shows the ampere-hour capacity and the PAM utilization to a 1-Volt cutoff at 25 C for these high rate discharges. The cell limiting current was measured at 3.25 A/cm^2 .

Constant current polarization curves were also obtained, as shown in Figure 8. Each of the data points in Figure 8 represents the cell voltage for a constant current discharge, measured after a fixed time interval from the start of the discharge. Four such intervals are shown for eight constant current discharges. For the given time intervals, the area resistivities range from .48 to .68 ohm-cm², or roughly twice the values assumed for our calculations of projected performance. Improvements in actual performance are expected upon optimization of the cell design.

VII POTENTIAL PROBLEMS

The sealed bipolar lead acid battery shares an important problem with other sealed batteries. It must be carefully designed in order to prevent gas leaks to the outside. Special attention must also be paid to preventing electrolyte leaks from cell to cell.

Another problem which may be unique to this design is that the light weight bipolar plates are not good heat conductors; the mean specific heat of this battery, however, will be considerably

higher than other lead-acid batteries, and likely higher than other batteries in general because of its high fraction of aqueous electrolyte and the fact that much of the lead is replaced by a plastic.

ACKNOWLEDGEMENT

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TABLE 1

PHYSICAL CHARACTERISTICS OF 2-LAYER BIPOLAR PLATES

Sample #	Weight (g/cm ²)	Thickness (mils)	Volume Resistivity (ohm-cm ²)
D-411-1	0.116	32	9.6
P1700-1	0.137	32	4.6
K-720-1	0.072	18	1.2
K-720-2	0.074	18	1.1
K-730-2	0.108	22	2.1
K-730-2	0.110	23	5.3
K-730-3	0.112	26	8.3
K-460-2	0.109	22	2.1
K-460-3	0.120	29	6.4
P1700-2	0.078	21	2.8
P1700-3	0.083	24	4.7
D-470-1	0.071	19	4.1

TABLE 2
COMPARATIVE CHARACTERISTICS OF ELECTROCHEMICAL COUPLES

Couple	E'oc (Volt)	r (ohm-cm)	M*** (Watts/cm)	Q/E (@2/3 E'oc)
Lead-Acid	2.10	1.12 (1)	3.93	0.45
Li(Al)-FeS	1.33	0.64 (2)	2.76	0.55
H2-O2	1.05*	0.50 (3)	2.20	1.11
Ni-Zn	1.72*	1.84 (4)	1.61	0.54
Ag-Zn	1.59*	1.84	1.37	0.75
Ni-H2	1.32*	1.84	0.95	0.80
Ni-Cd	1.30*	1.84	0.92	0.58
Na-S	2.08*	4.7 (5)	0.92	0.55
LiSOC12	3.32	47.6 (6)	0.28	0.68

Q/E is the ratio of thermal to electrical power at 2/3E'oc.

- (1) Value at 30 C
- (2) Value at 450 C
- (3) Value at 100 C
- (4) Value at 18 C
- (5) Value at 300 C
- (6) Value at 50 C

* Extrapolation from E - I curves

** Open circuit voltage used because of low activation polarization.

*** M = Figure of merit = $(E'oc)^2/r$

TABLE 3
PROJECTED 50 KW BATTERY CHARACTERISTICS

	Constant Current Discharge			
	1 sec*	5 sec*	10 sec	100 sec
No. of Cells	50	50	50	50
Cell Voltage Under Load	1.84	1.75	1.74	1.91
Cell Current, Amps	543	571	575	524
Case Dimensions				
Height	1.75"	2.0"	2.35"	3.55"
Width	9.7"	9.9"	10.0"	17.8"
Length	9.7"	9.9"	10.0"	17.8"
Battery Weight, Kg	2.5	3.6	5.4	33.3
Mean Specific Power kW/kg	20	14	9.3	1.5

* Current limited to 1.0 A/cm²

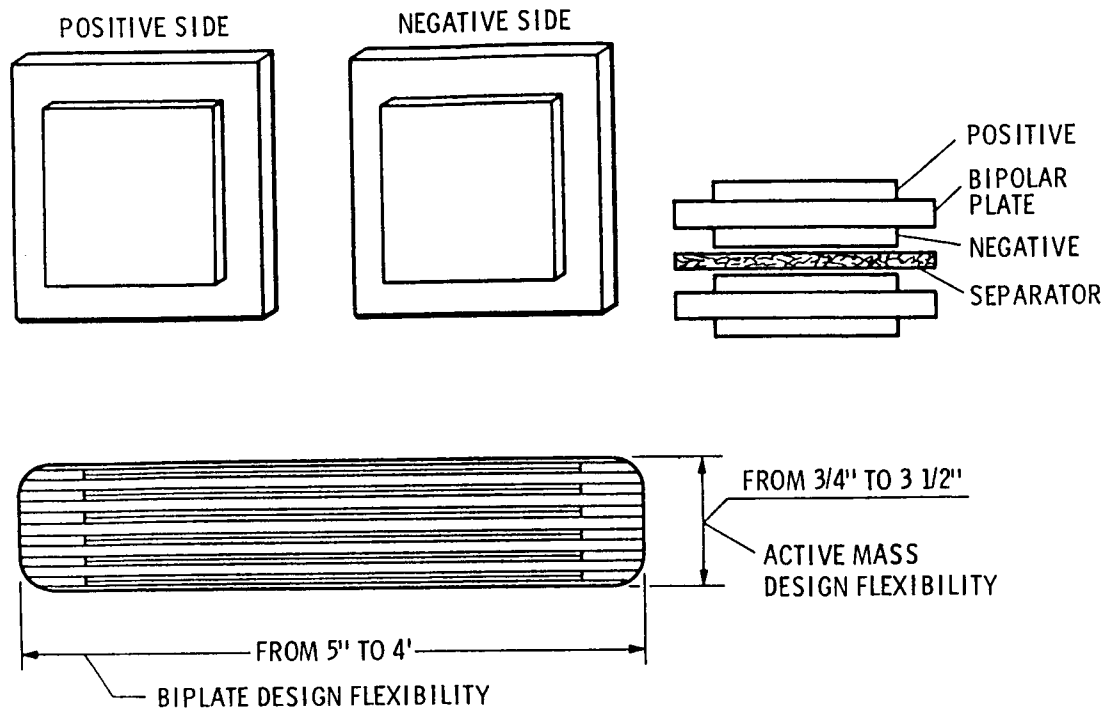


Figure 1. - Bipolar lead-acid battery.

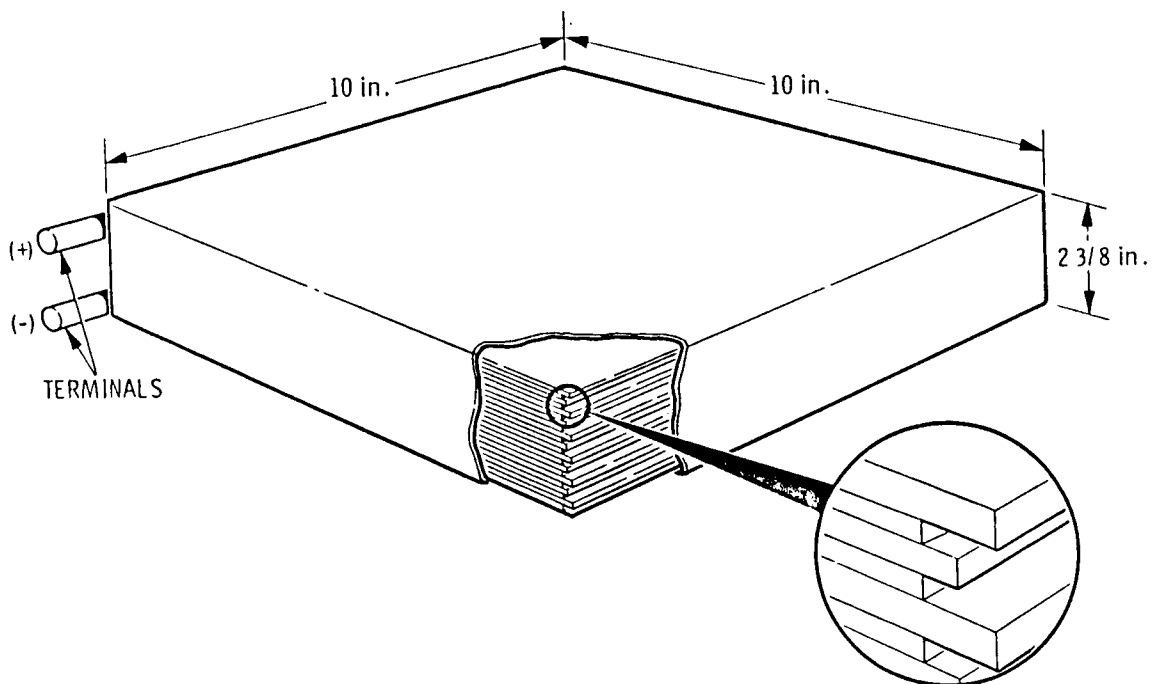


Figure 2. - 50-KW, 50-cell bipolar lead-acid battery. Discharge, 10 sec; weight, 12 lb.

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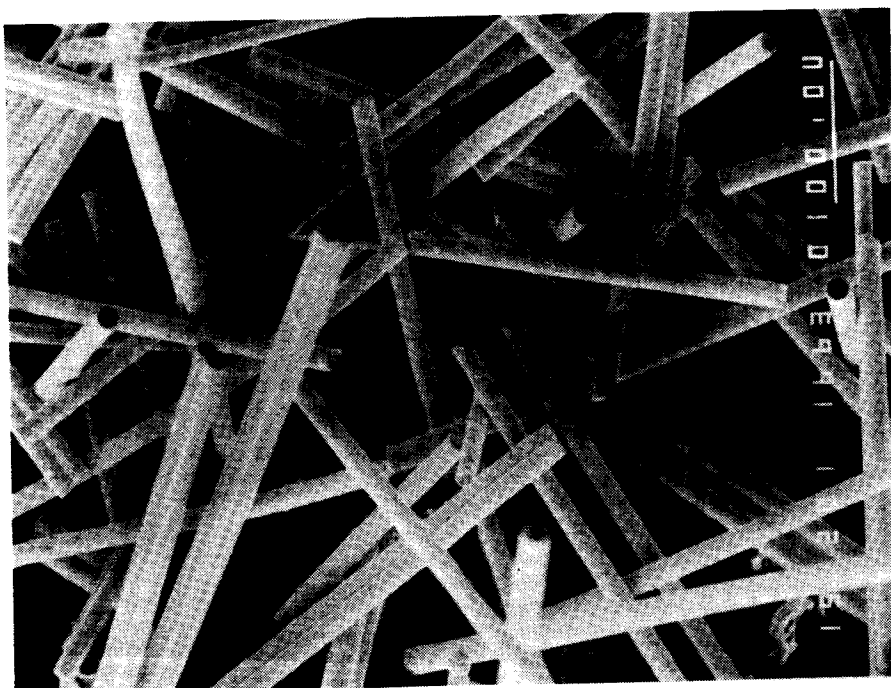
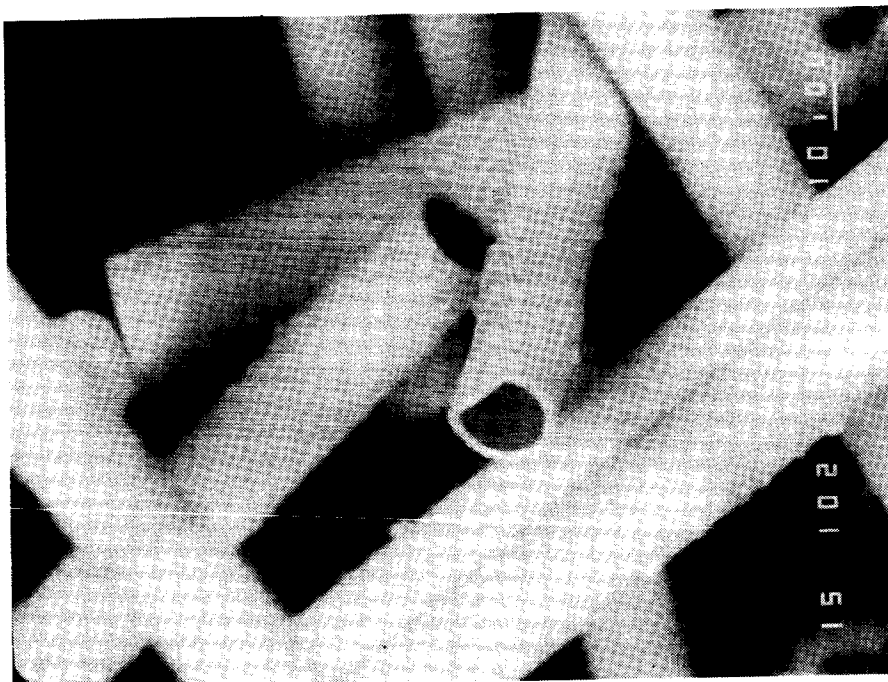


Figure 3. - S_nO_2 -coated glass fibers.

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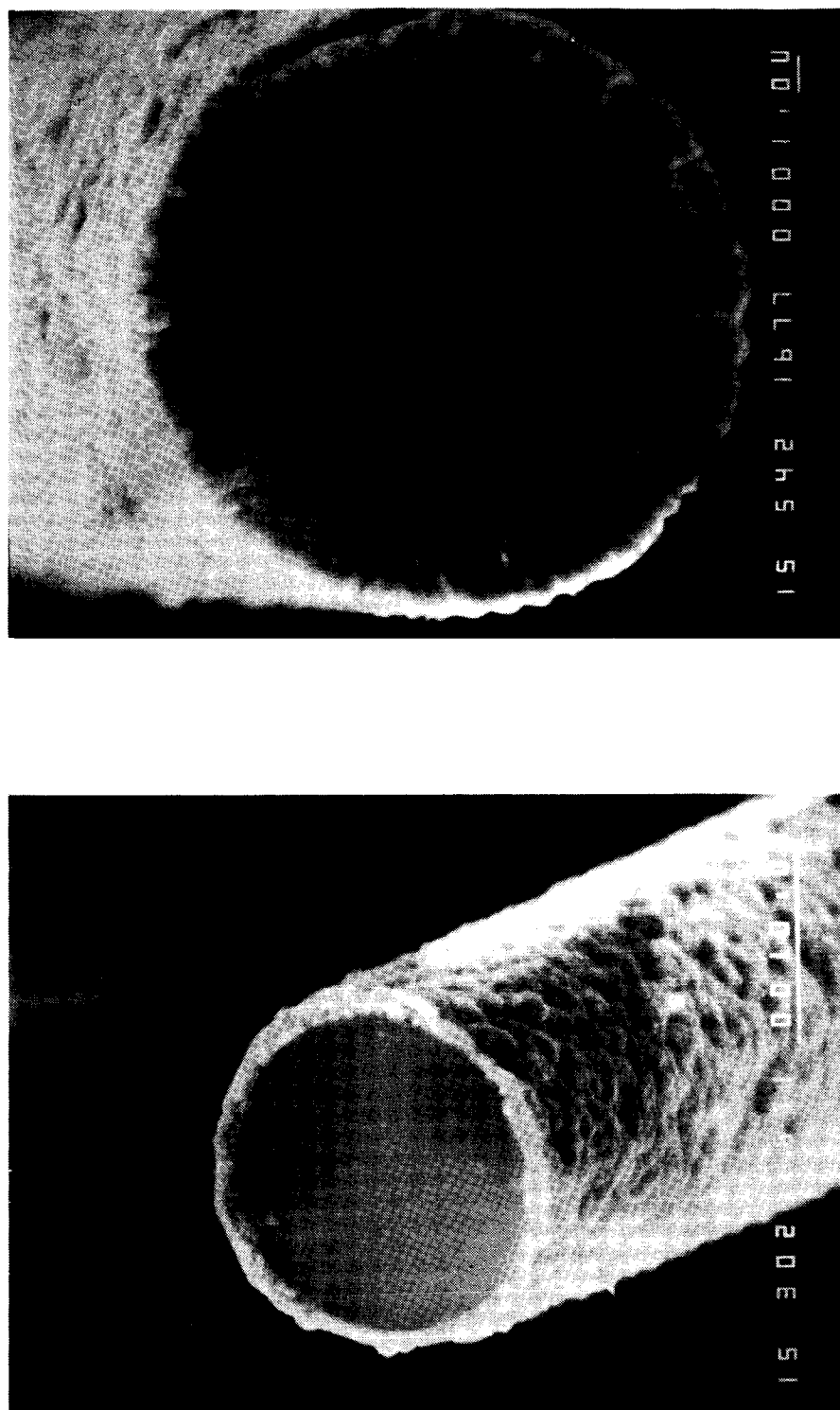


Figure 4. - SnO_2 -coated glass fibers.

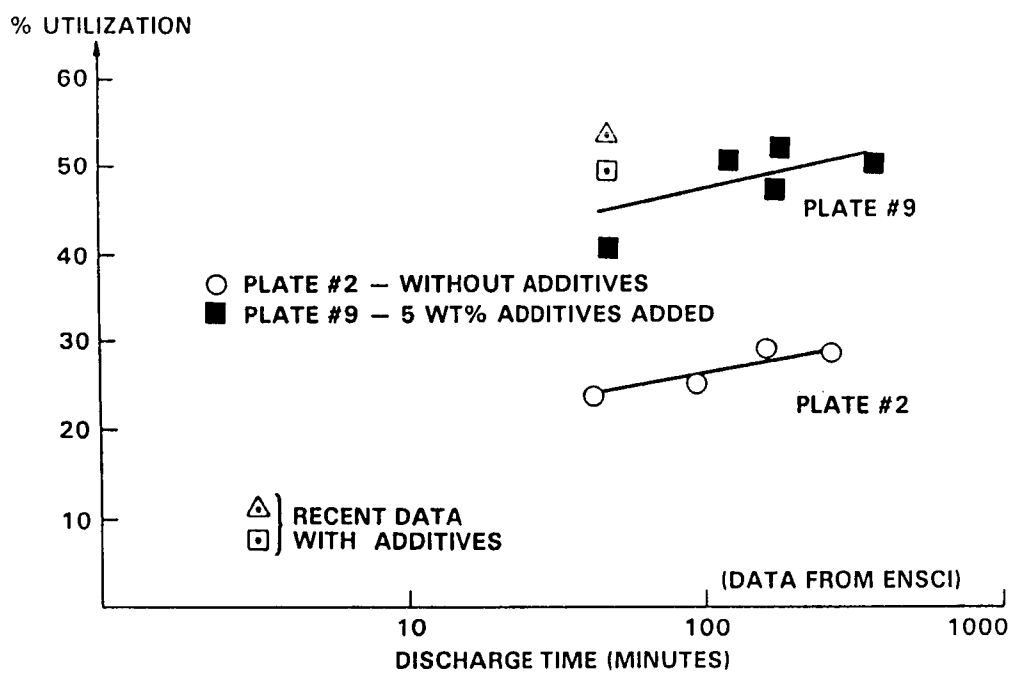


Figure 5. - Utilization efficiency of positive active material.

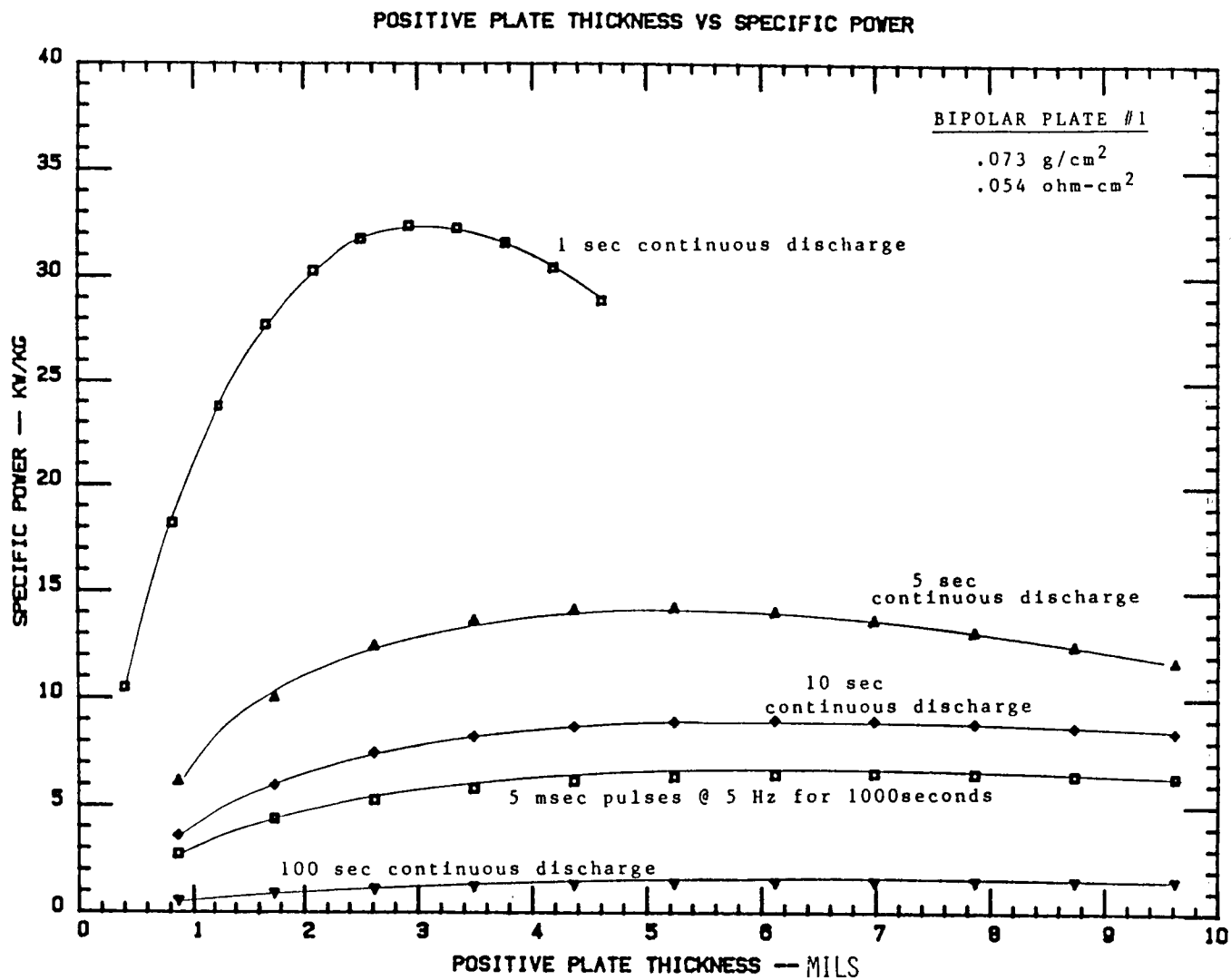


Figure 6. - Positive plate thickness vs specific power.

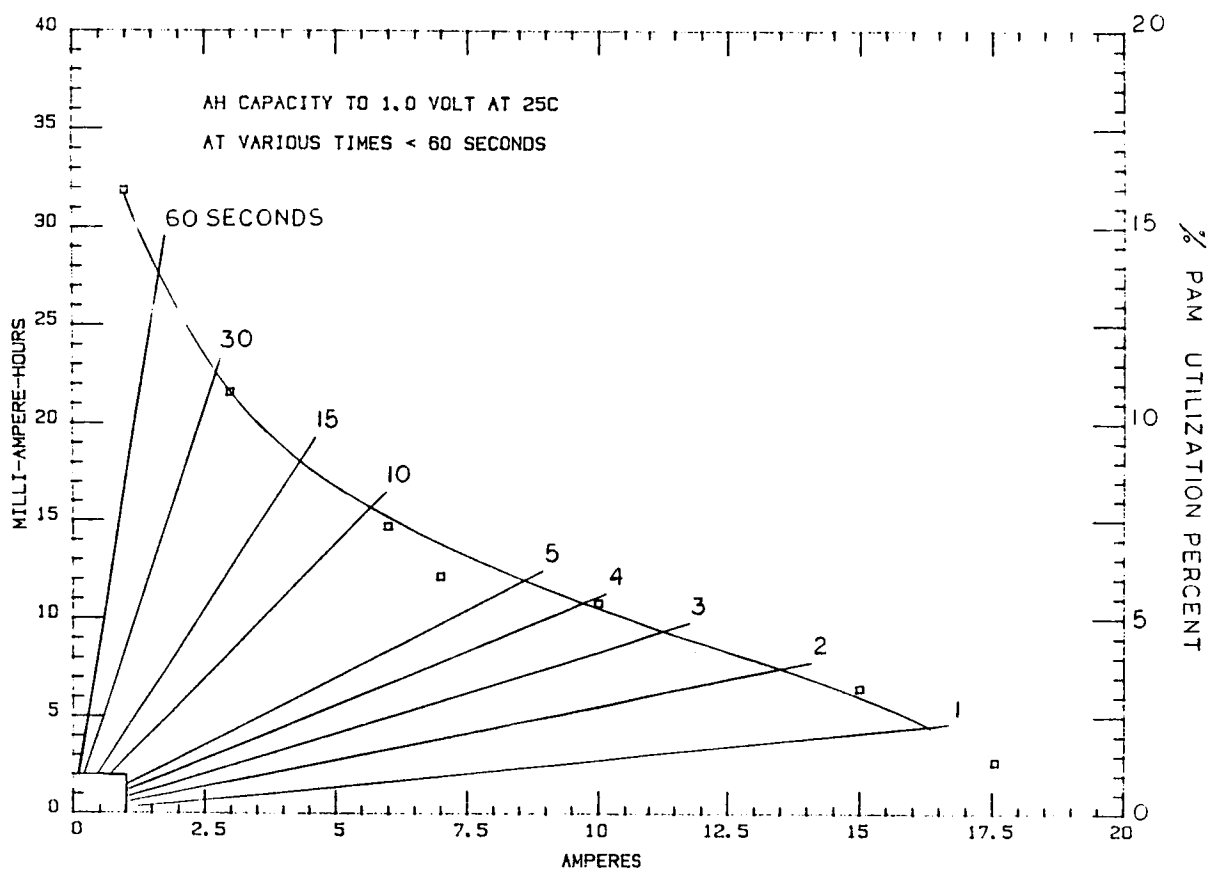


Figure 7. - Testing of monopolar cell with bipolar geometry.

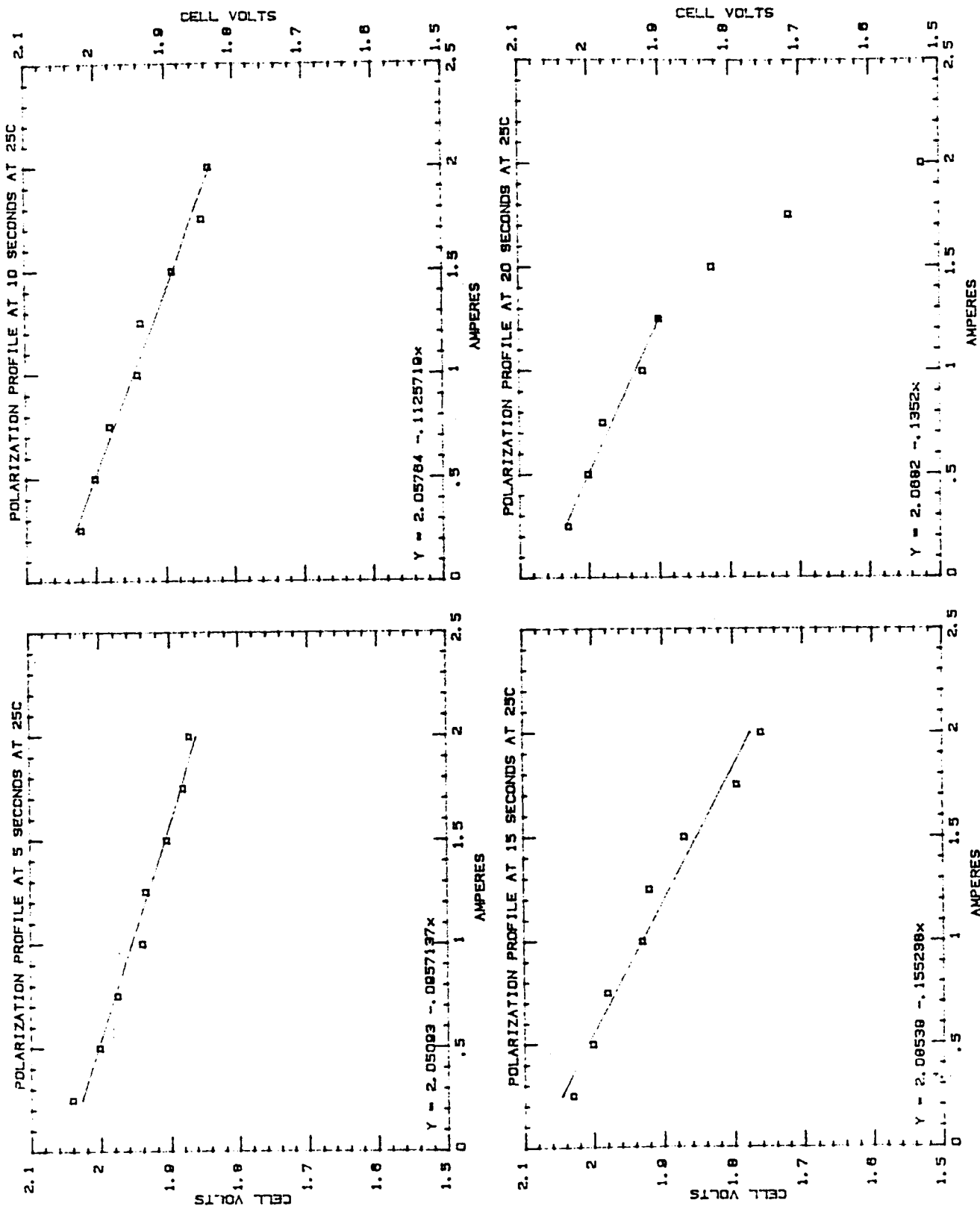


Figure 8. - Polarization curves for monopolar cell with bipolar geometry.